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(54) Title: MILDLY BASIC ACCELERATING SOLUTIONS FOR DIRECT ELECTROPLATING

(57) Abstract

Novel aqueous accelerating solutions and methods for their use in connection with direct electroplating of dielectric basis materials are disclosed and claimed. The accelerating solutions are mildly basic aqueous solutions including dilute concentrations of copper ions.

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MILDLY BASIC ACCELERATING SOLUTIONS FOR  
DIRECT ELECTROPLATING

REFERENCE TO RELATED APPLICATION

This application is a division and continuation-in-part of prior United States Application Serial No. 440,661 filed November 21, 1989.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention is directed to accelerating solutions for use in connection with the direct electroplating of dielectric base materials as well as with the electroless plating of such materials. More particularly, the present invention is directed to mildly basic aqueous accelerating solutions which contain copper ions for treating the surface of dielectric substrates prior to electroplating. The present invention is particularly well suited for use in connection with associated methods for directly electroplating metals onto the surfaces of non-conducting or dielectric substrates without the need for preliminary electroless plating, conversion coatings, solution additives, or conductive clips to initiate propagation of plating metal. The mildly basic accelerating solutions of the present invention are applicable to multi-layer laminated circuit boards and copper clad substrates and are particularly well suited to use in pattern plating processes and with non-clad substrates and molded circuitry. Moreover, the mildly basic accelerating solutions of the present invention eliminate substantial plating and manufacturing costs.

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Description of the Prior Art

Accelerating solutions are commonly used to improve the speed and quality of metallic plating processes. Numerous methods for the metallic plating of dielectric

surfaces are known in the art and have proven to be useful in the production of printed electrical circuit boards. Generally speaking, the metallic plating of dielectric surfaces is accomplished by first making the surface 5 catalytically receptive to electrolessly formed metal deposits followed by electrodeposition of a plating metal over the electrolessly formed conductive metal deposits. Though effective at producing conductive metal layers upon non-conducting substrates, such multi-step electroless 10 plating methods are expensive and limited in their application due to the chemical susceptibility of the electroless layer and the need for stringent process controls. Further limitations exist on the process of electroless plating because it requires the use of 15 extremely hazardous and toxic materials.

Efforts at overcoming these limitations and at reducing the associated expenses and health risks through the elimination of the electroless plating step have met with only partial success. Generally, these alternative 20 methodologies substitute additional steps such as coating the substrate with conductive materials in place of the electroless plating. Though direct plating of dielectric materials through the use of graphite coatings or conductive metal powder coatings in place of the electrolessly 25 deposited metal layers has been achieved these methods are equally cumbersome and carry their own disadvantages.

More specifically, early electroless plating catalyst systems consisting of palladium chloride and tin chloride in acidic solutions were developed in the late 1940's and 30 early 1950's. For example, U. S. Patent No. 2,702,253 (Bergstrom) disclosed a two step procedure in which the dielectric substrate was first sensitized by immersion in an acidic tin chloride solution followed by activation in a palladium chloride solution. Such catalytically 35 activated surfaces would promote the generation of an electrolessly formed metal deposit layer through the oxidation of suitable components contained in an

electroless plating bath. This initial electrolessly deposited conductive metal layer could be plated further through conventional electroplating. However, these two step catalyst systems had significant disadvantages.

For example, in the production of printed circuit boards having copper clad conductive surfaces on opposite sides of the insulating dielectric substrate it is a common practice to make electrical connections between the conductors on each side of the circuit board by forming holes through the board and then plating a conducting material on the surface of the "through holes" to interconnect the conducting layers. When utilizing the two step electroless deposition process to plate the surfaces of the through holes with a conducting metal it was found that the palladium chloride solution would produce an unwanted flash coating of palladium metal onto the copper clad surfaces of the substrate which subsequently had to be removed. As a result, this proved to be a wasteful and very expensive process.

Through holes are also utilized to interconnect the conducting layers of multi-layer laminated circuit boards having dozens of conductive layers separated by non-conducting substrate materials. Unfortunately, the acidic catalyst solutions utilized for electroless plating would also attack the black copper oxide layers of the multi-layer substrates, creating cavities or "voids" between the copper layer and the non-conducting layers which could become sites for chemical contamination and corrosion, thus interfering with the conductivity of the layers.

Improvements in the catalytic process involved the formation of a mixed palladium/tin catalytic system which combined the sensitization and activation steps in a single solution. An exemplary stem is disclosed in U. S. Patent No. 3,011,920 (Shipley). These single step catalytic baths were formed of aqueous solutions containing high concentrations of HCl in which varying amounts of palladium chloride and tin chloride were

A further limitation to this process is its inapplicability to modern pattern plating circuit board construction techniques. In pattern plating processes the electrodeposition of metal does not take place until after 5 the substrate has been imaged with a photo resist to form a circuit pattern. As a result, electroplated metal will not cover the entire surface of the substrate. Unfortunately, treatment of the conductive cladding of the substrate prior to application and development of the 10 photo resist utilizes chemicals found to dissolve or desorb the discrete metallic sites previously deposited on the through hole walls. As a result, directly electroplating the through holes is rendered impossible, making the methodology inappropriate for use with pattern 15 plating.

An alternative approach to direct plating was disclosed in European Patent No. 0,298,298A2 (Bladon). This process provided for the electroplating of a non-conducting surface after a conversion treatment which 20 converted an adsorbed colloid surface coating into a chemically resistant "conversion coating" which could function as a base for direct electroplating. A similar process was disclosed in United States Patent No. 4,810,333 (Gulla, et al). Though conversion coatings will 25 withstand the chemical treatments found in pattern plating techniques, these processes are as complex as electroless plating and utilize hazardous chemicals which are difficult and expensive to dispose of. An additional disadvantage of conversion coatings is the relatively high 30 current density required to achieve direct electroplating which limits these processes to plating large through holes.

With virtually all of these known electroless and direct metallic methods the utilization of an acceleration 35 step has been found to be beneficial. Generally, acceleration takes place prior to the final electrodeposition of the plating metal. Typically, the

catalytically treated surfaces of the substrate to be plated are treated through immersion in a strongly acidic or, to a lesser extent, a strongly basic accelerating solution. Following treatment the accelerated substrate 5 is rinsed with distilled water to avoid interference with subsequent plating steps. In both cases the accelerating solution functions to remove much of the protective tin component from the catalytically deposited palladium/tin film. This treatment renders the palladium catalyst 10 material adsorbed on the surface of the material more catalytically active towards the subsequent electroless metal plating.

In addition, prior art accelerators have been utilized to remove significant amounts of the 15 catalytically deposited activator or film from any copper surfaces present on copper clad circuit boards. Excess catalytically deposited film on the copper foil may create zones of poor adhesion where the subsequently 20 electroplated copper fails to adhere to the copper cladding. Additionally, traces of catalyst left on the copper foil may disrupt the flow of electricity on subsequently formed circuits making it difficult to predict circuit impedance with a high level of certainty which places a practical limit on the minimum size of 25 circuit components.

As those skilled in the art will appreciate, removal of tin from the catalytic activator deposited colloidal film and removal of catalyst from copper surfaces on copper clad circuit boards requires precise process 30 controls if these functions are to be accomplished without removing the palladium/tin catalyst from the dielectric substrate. Thus, known accelerating solutions must be monitored closely with respect to solution concentration, treatment time, temperature and agitation as well as to 35 the over accumulation of tin or copper in the solution.

Accordingly, it is a principle object of the present invention to provide novel accelerator solutions which

circuits having unusually small diameter through holes. An additional advantage of the present invention is that the micro-fine catalytic colloid solution is non-acidic and therefore is particularly well suited for use with 5 multi-layer printed circuit boards as it will not attack the copper oxide layers commonly found therein.

More particularly, the method of the present invention comprises the step of directly electroplating a non-conductive substrate having at least a portion of its 10 surface coated with a strongly adsorbed, uniform conductive layer of micro-fine colloidal metal. This can be accomplished by treating the surface of a non-conducting substrate with a solution of a micro-fine colloidal dispersion of palladium and tin to form a 15 uniform, conducting layer of deposited colloidal material followed by the step of electroplating directly over this conductive layer. Preferably, in accordance with the teachings of the present invention, the micro-fine conductive colloidal layer will be treated with a mildly 20 basic accelerating solution incorporating copper ions prior to the electroplating step. The catalytically treated and accelerated dielectric substrate can be dried and manipulated following catalytizing treatment without desorbing or otherwise damaging the colloidal conductive 25 layer and therefore may be incorporated into pattern plating processes prior to direct electroplating.

The micro-fine colloidal catalyst solution is formed in a multi-step process utilizing a non-acidic, saturated aqueous salt solution. Preferably, the salt solution will 30 be saturated with sodium chloride or an alternative halide salt. The solution is divided into two portions and an effective amount of a noble or precious metal salt is dissolved in the first portion and a relative molar excess of stannous chloride or other halide salt is dissolved in 35 the second portion. The solutions are then combined and reduced in volume to form a supersaturated concentrate of highly dispersed, uniform, stable, micro-fine colloidal

particles. Unlike the prior art catalyst solutions which must be aged and decanted to remove large colloidal particles prior to use, the supersaturated concentrate of the present invention can be stored indefinitely without 5 particulate settling and does not require decanting.

The concentrated catalyst solution is then preferably diluted by a factor on the order of 10° to 1 with an aqueous salt solution to prepare a catalytic bath for dipping the substrates to be plated. Treating the dielectric substrates with the catalyst solution so produced 10 deposits a strongly adsorbed, uniform, conducting layer of micro-fine colloidal metal onto the surface of the substrate. Because the colloidal layer is sufficiently conductive the treated substrate can be utilized as an 15 electrode in an electrolytic cell containing a dissolved plating metal. Passing a current between the catalytically treated substrate electrode and a second electrode immersed in the electrolyte solution directly electroplates the plating metal onto the surface of the 20 substrate.

The mildly basic accelerating solutions are preferably formed by mixing from 100 to 400 grams per liter (g/l) of a wide variety of alkaline substances including NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in distilled water. 25 To this solution a small amount of copper ions, preferably in the form of CuSO<sub>4</sub> is added. The mildly basic accelerating solutions so produced are very stable and operate over a wide range of temperatures and treatment times. Additionally, because these alkaline solutions are 30 not aggressively removing tin or copper from the treated substrates it is not necessary to monitor the accelerating baths. Thus, the accelerating treatment simply involves immersing the catalytically treated substrates into the accelerator solution of choice with agitation at room 35 temperature or slightly above (for example, elevated temperatures of approximately 45°C to 65°C may be

utilized) for a period of approximately ten minutes followed by a brief rinse with distilled water.

It should be emphasized that the strongly adsorbed conducting layer of micro-fine colloidal metal deposited 5 on the surface of the treated substrate is remarkably stable and durable, even after acceleration. Accordingly, it is possible to further process the treated substrate prior to electroplating without damaging the strongly adsorbed conducting layer of colloidal metal. Such 10 further processing can involve the imaging steps commonly associated with modern pattern plating techniques. Since the strongly adsorbed layer of catalytic metal is conductive, the method of the present invention is particularly well suited for utilization with non-clad 15 substrates and molded circuitry where the initial substrates do not incorporate a layer of bonded copper foil.

An additional benefit of the method of the present invention is that direct electroplating of the strongly 20 adsorbed conducting catalytic layer can take place at significantly reduced current densities relative to conventional substrate plating. As a result, the method of the present invention makes it possible to plate smaller diameter through holes without filling the holes 25 with conductive metal. This feature is advantageous for attaching components to the plated substrate with finer leads and for producing printed circuit boards having higher circuit densities than those previously attainable with the large diameter through hole prior art plating 30 processes.

Further objects, features and advantages of the method of the present invention and the catalytically or electrically plated substrates so produced will become apparent to those skilled in the art from a consideration 35 of the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

In a broad aspect, the method of the present invention is based upon the surprising discovery that a catalytic noble or precious metal solution such as a palladium chloride/tin chloride solution can be prepared 5 in a non-acidic aqueous salt solution. More importantly, modifications and improvements to these solutions in accordance with the teaching of the present invention produce catalytic colloidal particles that are unusually small and well dispersed relative to those of known or 10 pre-existing catalytic solutions and, as a result, they are extremely effective in adsorbing onto solid surfaces, producing uniform conducting catalyst layers.

Of equal importance, it was surprisingly discovered that it is possible to enhance the physical continuity and 15 resultant conductivity of the adsorbed catalytic film by treatment with a mildly basic or alkaline accelerator bath incorporating a small quantity of copper ions. These copper ions are adsorbed onto the catalyst film such that they bridge any gaps between the micro-fine palladium/tin 20 colloids. Additionally, it is believed that the mildly basic accelerating solutions also slightly dissolve and redeposit the colloidal particles to form a more continuous or nearly continuous conductive film or particle network. This treatment significantly enhances 25 the conductivity of the catalytically deposited activator film in direct contrast to the prior art accelerators which produce isolated, non-conductive, discrete catalytic sites.

Non-acidic catalytic solutions are the general 30 subject matter of the Inventor's co-pending International Application No. PCT/US 89/00102, International Filing Date January 11, 1989, United States Patent Application Serial No. 239,935, Filing Date September 2, 1988, and Japanese Patent Application Serial No. 63/3133, filed January 12, 35 1988. Refinement to this general class of non-acidic palladium/tin catalyst solutions has resulted in the production of micro-fine catalytic colloidal particles

which preferentially adhere to the surface of non-conducting substrates with such uniformity and strength that the metallic surface layer so formed is sufficiently conductive to permit direct electroplating without the  
5 need for plating solution additives, conversion coatings, or electroless metal deposition.

What is more, the method of the present invention is particularly applicable to multi-layer circuit boards and copper clad dielectric substrates because the strong  
10 adsorption of the micro-fine conductive colloidal catalyst layer takes place in the absence of appreciable amounts of HCl and thus does not attack the black copper oxide layers exposed along the surfaces of the circuit board through holes.

15 Moreover, it should be emphasized that the conductive micro-fine colloidal layer deposited onto dielectric substrate surfaces through the method of the present invention is exceptionally durable. As a result, prior to direct plating, the micro-fine colloidal layer can withstand  
20 the processing steps commonly associated with pattern plating and imaging, making the method of the present invention and the circuit boards so produced particularly well suited to contemporary pattern plating processes as well as to use with non-clad substrates and  
25 molded circuitry.

Additionally, it will also be appreciated by those skilled in the art that the method of the present invention effectively eliminates the need for costly electroless metal plating methodologies and the associated  
30 processing limitations while actually improving the metal plating so produced. Moreover, unlike the prior art methodologies, the present invention eliminates electroless plating while actually decreasing the total number of steps required for effective metal deposition. As an  
35 added benefit, eliminating the need for electroless plating, prior art conversion coatings, or solution additives also eliminates the complexity, hazards and cost

associated with monitoring, controlling and disposing of the costly solutions associated with these prior art processes. When coupled with the economies available through pattern processing techniques the method of the 5 present invention can eliminate up to 40% of the prior art manufacturing costs normally associated with the production of printed circuit boards.

For purposes of this application, the micro-fine colloidal layer deposited upon the surface of dialectic 10 substrates in accordance with the teachings of the present invention will be referred to as "conductive". By this it is meant that these deposited metal layers exhibit an exceptionally low electrical resistance on the order of from one to tens of ohms, typically ranging between 15 approximately 1 ohm and 50 ohms as measured from side-to-side through the through holes. In direct contrast to this relatively high conductivity, the prior art semi-colloidal palladium film layer disclosed in the direct plating methodology of United States Patent 3,099,608 20 (Radovsky, et al) showed a resistance of approximately  $8 \times 10^7$  ohms. Similarly, even the most highly conductive catalytic metal layers of the prior art are unable to support direct electroplating of metal on multi-layer boards because of high electrical resistance on the order 25 of 500 ohms to 1,000 ohms. Based upon electrical conductivity alone, it is clear that the preferentially adsorbed micro-fine colloidal layers produced through the method of the present invention are unique and are significantly more uniform and complete than those of the 30 prior art.

The method of the present invention is suitable for the plating and manufacture of variety of commercial articles where a metal deposit is desired over the surface of a non-conductor. Typical non-conducting substrate 35 materials known in the art to exhibit inadequate conductivity for direct electroplating include plastics, resins, and epoxy materials such as the glass fiber filled

epoxy substrates commonly used in the manufacture of printed circuit boards. In that the method of the present invention is especially well suited for the manufacture of printed circuit boards, the exemplary embodiments discussed herein will be directed to the production of printed circuit boards. However, it should be emphasized that these exemplary embodiments of the present invention are illustrative only and in no way limit the scope of the present invention to circuit board manufacture alone.

Similarly, the exemplary embodiments of the present invention discussed herein are not limited to the utilization of palladium as the catalytic metal. Rather, other catalytic metals including noble and precious metals may be employed in place of the palladium discussed in detail herein. However, as those skilled in the art will appreciate, palladium and palladium chloride are readily available and have broad applicability and relatively low cost when contrasted to other effective noble or precious metals. Accordingly, while the use of palladium metal catalytic solutions are preferred, the present invention is not limited to the use of palladium.

In contrast to the palladium/tin catalytic solutions of the prior art which are typically formed in concentrated hydrochloric acid solutions, the exemplary micro-fine catalytic colloids of palladium/tin utilized to practice the method of the present invention are formed in a non-acidic, supersaturated, aqueous salt solution. For example, an exemplary micro-fine colloidal solution for use in accordance with the teachings of the present invention can be produced as follows: first, 1Kg of sodium chloride is added to 3 liters of water and heated to approximately 60°C to form a saturated solution. Next, 1Kg of stannous chloride crystals are mixed with a sufficient volume of this saturated salt solution to form 1.9 liters. A slight amount of heat may be necessary to completely dissolve the stannous chloride into this solution. For example, heating the solution to

approximately 20°C to 30°C with occasional stirring is generally sufficient. Next, in a separate container, 20g of powdered palladium chloride are added to 200ml of the saturated salt solution. This palladium solution is 5 stirred and heated to a temperature between about 40°C to 60°C until the palladium chloride is completely dissolved. The dissolved palladium chloride salt solution is then added to the stannous chloride salt solution with stirring and heat being applied to raise the temperature to 10 approximately 80°C plus or minus 2°C. Preferably, this temperature is maintained for approximately one hour to evaporate approximately 5% to 10% of the contents of the solution, creating a supersaturated solution. Following this concentration step the solution is allowed to cool to 15 produce approximately two liters of supersaturated, concentrated micro-fine colloidal palladium/tin salt solution.

It should be noted that the aqueous salt solution is preferably formed of sodium chloride at or near supersaturated concentration. However, other halide salts are contemplated as being within the scope of the present invention though sodium chloride is preferred because of its ready availability and low cost. Additionally, the preliminary salt solution need not be supersaturated as 20 near saturated solutions are sufficient. However, supersaturation will occur during the heating process, as 5% to 25 10% of the water is evaporated.

A modified micro-fine colloidal catalyst solution can also be prepared utilizing the following technique. As 30 with the previously described salt solution, 1Kg of sodium chloride is added to 3 liters of water and heated to approximately 60°C to form a supersaturated solution. Then, prior to the addition of the palladium chloride and 35 stannous chloride previously described, 2 liters of the saturated salt solution are transferred to a separate container into which 3g of an aromatic aldehyde such as lignin vanillin (in crystallin form) are added. The

elevated temperature and stirring are maintained for approximately 30 to 40 minutes until the aldehyde is completely dissolved. This aromatic aldehyde salt solution is then utilized to form the micro-fine palladium 5 tin catalytic solution as previously described. The aromatic aldehyde serves to protect the palladium/tin colloids and to prevent them from agglomerating or coagulating in the salt solution.

Though not essential to the practice of the present 10 invention, the addition of an aromatic aldehyde has the added benefit of further enhancing the adsorption characteristics of the catalytic solution and hence the durability and conductivity of the catalytically deposited layer. It is theorized that the aromatic aldehyde 15 palladium/tin colloids are hydrophobic as well as polar and that they therefore preferentially adsorb on the solid surface of the substrate in a manner which leaves the aldehyde closest to the substrate and the tin closest to the liquid with the palladium in between. The colloidal 20 layer thus deposited is both more tightly adsorbed to the substrate and also more easily accelerated because the tin which is stripped during acceleration is closest to the accelerating solution.

The micro-fine catalytic colloidal solution concentrates so produced are preferably diluted prior to use in accordance with the teachings of the present invention. An exemplary dilution factor of approximately 30 to 1 is preferred though other concentrations and ultra-dense catalyst solutions are also contemplated as being within 25 the scope of the present invention. Preferably, the concentrated micro-fine catalytic colloid solution will be diluted on the order of 10 to 1 in a saturated salt solution. No other additives or stabilizers are needed to form this dilute solution. However, a small amount of HCl 30 (approximately 4 ml) or H<sub>2</sub>SO<sub>4</sub> (approximately 0.5 ml) may be added to prevent the formation of an oxidized tin layer on the subaerial surface of the solution if desired.

Alternatively, it is also possible to dilute the concentrated micro-fine catalytic colloid solution in an approximately 5% to 10% salt solution containing from about 0.0005 to 0.001 volume percent sulfuric acid as a 5 stabilizer. Those skilled in the art will appreciate that while these exemplary solutions possess previously unattainable degrees of micro-fine colloidal distribution, they will not require unusual monitoring or control relative to existing catalytic solutions. Additionally, 10 it should be noted that, where desired, the amount of stabilizing acid that may be added to the catalytic solutions is insufficient to chemically interact with black copper oxide.

The micro-fine catalytic colloidal solutions so 15 produced are utilized in accordance with known catalysis procedures to produce the unique conductive colloid layer of the present invention. For example, the surface of a non-conducting substrate to be plated in accordance with the teachings of the present invention can be exposed to 20 the catalyst solution through immersion in a solution bath for a period of time ranging from approximately 5 to 10 minutes, preferably at temperatures varying between approximately 35°C to 55°C. Additionally, where desired the processing sequence may involve immersion in a 25 catalyst pre-dip solution comprising an aqueous salt solution compatible with the catalytic solution but lacking the micro-fine colloid. As is known in the art, the utilization of a pre-dip solution prevents the contamination of the catalyst by rinse water or other 30 solutions which may be clinging to the surface of the substrate to be treated. This further exemplifies the unique compatibility of the method of the present invention to existing plating technology. An added benefit is realized by the presence of the vanillin in the 35 pre-dip in that it promotes better adsorption of the micro-fine colloids by initiating a partial polarization of the substrate surface.

Accordingly, in its broadest aspect the method of the present invention comprises directly electroplating a conductive metal onto an electrically conductive micro-fine catalytic colloid layer deposited onto the surface of 5 the non-conducting substrate to be plated. Electroplating of the treated substrate can be accomplished utilizing the conventional electroplating technique of passing a current between two electrodes immersed in an electrolyte bath containing a dissolved plating metal. Because of the 10 unique conductivity of the preferentially adsorbed, substantially uniform, conducting layer of micro-fine colloidal metal provided on the surface of the dielectric substrate through the method of the present invention it is possible to directly utilize the treated substrate as 15 one of the electrodes in the plating bath. In this manner, the treated substrate is directly electroplated with a layer of metal without the need for a prior electroless plating treatment, conversion coating, or plating solution additives.

Because the present invention allows the use of simple plating solutions without the need for additives, an exemplary plating solution for practicing the method of the present invention can be produced as follows: into each liter of distilled or deionized water a mixture of 80 20 grams copper sulfate, 180 grams of sulfuric acid, and 30 mg chlorine are dissolved. This produces a typical 25 electroplating solution comprising an aqueous acid solution of the metal desired to be plated. Preferred electroplating metals are copper and nickel, though any 30 desired metal may be directly electroplated in accordance with the teachings of the present invention.

An unprecedented advantage of the method of the present invention is its ability to directly electroplate non-conducting substrates utilizing substantially lower 35 current densities than were previously possible with other dielectric plating methodologies. For example, electroplating current density can vary through a range of from

approximately 0.25 amps through 5.0 amps per  $\text{dm}^2$ , when plating the catalytically treated substrates of the present invention. As a result, the method and treated substrates of the present invention effectively enable the 5 production of circuit boards having unusually small diameter through holes to be plated without filling the hole with conductive metal. For example, it is easily possible to plate through holes having diameters in the range of 0.15 mm. Thus, in contrast to prior art plating 10 techniques wherein a through hole aspect ratio of hole depth to hole diameter of 10 to 1 is normal, the method of the present invention routinely and easily plates through holes having an aspect ratio of greater than 20 to 1. As those skilled in the art will appreciate, reducing the 15 size of circuit board through holes facilitates the production of higher circuit density devices which were either impractical or inoperative utilizing prior art techniques.

An additional advantage of the present invention is 20 that direct electroplating is accomplished with simple copper electroplating solution which puts a softer copper deposit on the electroplated substrate. As a result the plated substrates of the present invention are less brittle than those produced through known direct plating 25 and electroless plating methodologies. They are also less prone to cracking because of thermal shock and generally more durable than prior art substrates.

In all other aspects, electroplating the treated substrates of the present invention is generally conventional. For example, the simple plating solution bath used is preferably maintained at a temperature ranging between approximately 25°C and 30°C. Additionally, electroplating should be continued for a sufficient period of time to form a deposit of desired thickness. 35 Typically, desired circuit board thicknesses range from approximately 0.5 mils to 2.0 mils. A plating time of from approximately 1 to 90 minutes would be sufficient to

obtain a deposit of the preferred thickness within the preferred range of plating current density. However, unlike prior art electroplating methodologies wherein pealing or cracking of the plated metal may occur, the 5 electroplated deposits formed by the method of the present invention are strongly bonded to the surface of the non-conductive substrate, free of defects, and uniformly thick as a result of the superior properties of the uniformly deposited catalytic micro-fine colloidal layer. Thus, the 10 bond strength of the electroplated metal is sufficient to withstand solder shock testing as conventionally used in printed circuit board manufacture.

An additional unusual feature of the present invention is the ability to treat the catalytically 15 deposited conducting layer of micro-fine colloidal metal so produced with a mildly basic accelerating solution prior to electroplating. As those skilled in the art will appreciate, conventional plating accelerating solutions are generally strongly acidic or, to a lesser extent, 20 strongly basic solutions. However, the unique properties of the treated substrate of the present invention allow the use of mildly basic accelerating solutions such as dilute sodium or potassium hydroxide solutions or sodium or potassium carbonate solutions. Preferably, these 25 accelerating solutions will be formed by the mixing or dissolution of alkaline salts such as NaOH, KOH,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$  in distilled water to a concentration ranging from approximately 100 to 400 g/l. To this solution a small amount of copper ion containing solution is added.

30 For example, preferred exemplary mildly basic accelerating solutions can be formed by dissolving anywhere from 50 to 400 grams or more of the alkaline substance or substances of choice per liter of distilled water. Then, to each liter of this solution approximately 35 2ml of an exemplary copper ion containing solution formed by dissolving approximately 100g of  $\text{CuSO}_4$  in one liter of 10%  $\text{H}_2\text{SO}_4$ . Alternatively, a preferred accelerating

solution for use in accordance with the teachings of the present invention is an aqueous solution of approximately 200 grams per liter of sodium carbonate. The catalyzed substrate of the present invention can be treated through 5 immersion in a bath of such an accelerator solution, preferably at a temperature of approximately 50° for a period of approximately ten minutes with agitation. Following acceleration treatment, the substrate should be rinsed with distilled water to avoid interference with 10 subsequent treatment steps.

As those skilled in the art will appreciate, it is not uncommon for copper ions to naturally become incorporated into accelerator solutions when treating parts which are clad with copper. Nonetheless, in 15 accordance with the teachings of the present invention, purposefully adding copper ions to the accelerating solution provides the additional benefit of intentionally adsorbing the copper ions onto the colloidally deposited film to enhance the density and conductivity of the film. 20 Additionally, incorporating the copper ions in the accelerating solution is particularly important when treating unclad dielectric substrates where copper ions may not be desorbed into the solution.

In addition, the treated substrates of the present 25 invention are sufficiently strong to physically and chemically resist treatment solutions commonly used in pattern plating processes. As is known in the art, pattern plating involves drying and cleaning the dielectric substrate boards prior to applying and imaging 30 a photoresist film to obtain a desired circuit pattern mask. Imaging the photoresist pattern also involves exposing the substrate to reactive developing and etching solutions prior to electroplating. Prior art catalytic layers are unable to withstand such treatment and will 35 commonly desorb from the surface of a treated substrate making it impossible to electroplate.

A further understanding of the present invention is presented in the following non-limiting examples.

EXAMPLE 1

Direct Panel Electroplate Using Sodium Carbonate Accelerator

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A conventional printed circuit board substrate formed of glass fiber and epoxy clad with copper on both surfaces and provided with 8 mil through holes was cleaned, conditioned and dried as known in the art. Basically, the 10 substrate was immersed in a commercial cleaning solution identified as Shipley 1175 Cleaner Conditioner at a temperature of 80°C for ten minutes followed by a water rinse, soft bristle brush polishing to remove particles and oven drying at 180°C for 60 minutes. The copper 15 surfaces were micro-etched through immersion in a solution of sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) (200g/l) and sulfuric acid (5%) at room temperature for one minute followed by a distilled water rinse.

In accordance with the teachings of the present 20 invention, the prepped substrate was immersed in a pre-dip solution of saturated sodium chloride to which vanillin had been added (0.5g/l) at 45°C for ten seconds followed directly by immersion in a palladium/tin micro-fine colloidal catalyst solution prepared as discussed above. 25 Briefly, 35 ml of the concentrated, non-acidic saturated aqueous palladium/tin micro-fine colloidal catalyst was diluted with approximately 1 liter of a saturated sodium chloride solution containing 0.5g/l vanillin and 4ml/l of hydrochloric acid. The dilute solution was heated to 45°C 30 and the substrate was immersed into the catalytic solution bath for eight minutes followed by a rinse with distilled water for eight minutes. The catalytically treated substrate was then immersed in a mildly basic accelerating solution of 200g/l of sodium carbonate at 50°C for ten 35 minutes followed by a water rinse. The treated substrate was electroplated from a simple acid copper electroplating bath made by mixing copper sulfate (80 grams), sulfuric

acid (180 grams) and chlorine (30m) to each liter of copper electroplating bath. The plating current density was 0.5 to 2.0 amps per square decimeter at a temperature of 28°C for one-half to one hour. Those skilled in the art will appreciate that amperage and plating time will vary depending on the size of the through holes and the desired thickness of the electroplated copper layer. Following electroplating the plated substrate was rinsed with distilled water. The plated substrate had a uniform, defect free layer of electroplated copper material approximately 1 mil thick.

EXAMPLE 2

Direct Panel Electroplate Using Potassium Hydroxide Accelerator

An identical dielectric substrate was treated as in Example 1 to form a catalytically deposited micro-fine conducting colloidal layer. Following catalysis, the treated substrate was immersed in a basic accelerating solution of potassium hydroxide (200g/l) at 50°C for ten minutes, followed by a water rinse. Electroplating was accomplished as described in Example 1 with comparable results.

EXAMPLE 3

Direct Pattern Electroplating Using Permanganate Treatment and Potassium Hydroxide Accelerator

A copper clad substrate identical to that utilized in Examples 1 and 2 was immersed in a solution of potassium permanganate (50g/l) at a temperature of 45°C for six minutes, followed by a distilled water rinse. The through hole walls were cleaned and conditioned by immersing the substrate in a commercially prepared cleaner conditioner (Shipley 1175) at 80°C for ten minutes, followed by a water rinse. The copper surfaces were then micro-etched by immersing the substrate in a solution of sodium persulfate (200g/l) and sulfuric acid (5%) at room

temperature for one minute followed by a distilled water rinse. The substrate was pre-dipped and catalyzed as in Example 2 to form a catalytically deposited, micro-fine conducting colloidal layer.

5 Prior to electroplating a photoresist was applied and imaged as follows: the catalytically treated substrates were dried and cleaned and a film of photoresist (Riston 3015 available from E. I. DuPont De Nemours and Company of Willmington, Delaware) was applied at an application  
10 temperature between 98°C and 110°C and at a speed of from one to three feet per minute. Fifteen minutes following the application of the film the photoresist film was exposed to a source of activation energy through a master to obtain the desired circuit pattern at an exposure of  
15 40mJ/cm. Fifteen minutes later the imaged photoresist was developed by placing the substrate in a spray chamber utilizing a solution consisting of five pounds of sodium carbonate and one gallon of butyl carbitol per sixty gallons of developer and developed at a temperature of  
20 85°C for one minute.

The imaged substrate was then immersed in a solution of sodium persulfate (220g/l) and sulfuric acid (5%) at room temperature for fifteen seconds to micro-etch the copper surfaces prior to rinsing with distilled water.  
25 The substrate was then electroplated as described in the previous examples.

It should be noted that for commercial applications of completed pattern printed circuit boards, the plated boards produced in the foregoing example would require the  
30 additional steps of solder plating, photoresist removal, and copper surface etching. However, these steps would be unaffected by the direct pattern plating process of the present invention.

A copper clad dielectric substrate was electroplated through the previously described methodology of Example 3. However, the catalyst utilized to form the conductive micro-fine colloidal metal layer was formulated to contain 5 15g/l of palladium chloride and 600g/l of stannous chloride. The plated substrate so produced exhibit a strongly bonded, uniform electroplated layer of copper approximately 1 mil thick.

10

EXAMPLE 5Direct pattern plating Utilizing Permanganate Treatment and Sodium Carbonate Accelerator

A copper clad substrate identical to that utilized in the previous examples (1-3) was immersed in a solution of 15 potassium permanganate (30 c/l) and caustic soda (20 g/l) at a temperature of 40°C for 7 minutes, followed by a distilled water rinse. The through hole walls were cleaned and conditioned as in Example 3, except that the immersion time was shortened to 7 minutes. Again, this 20 step was followed by a water rinse.

The substrate was then immersed in a pre-dip of saturated sodium chloride similar to that of Example 1, except that 1.0 g/l of vanillin were used and the HCl was omitted. Pre-dipping was followed immediately by immersion in an activator solution made by mixing 45 ml of the concentrate with approximately 1 liter of the pre-dip solution containing no HCl and 1.0 g/l of vanillin. Immersion was continued at 45°C for 10 minutes. The treated substrate was then accelerated by immersion in a 25 sodium carbonate water rinse. Following acceleration the resistance was measured at 1.3 ohms.

The accelerated substrate was then stabilized by immersion in a 10% solution of H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at room temperature for 5 minutes. Following the stabilizing acid rinse, the 35 substrate was imaged as described in Example 3. The patterned substrate was then wetted by immersion in a 3% solution of Sodium Carbonate at room temperature for 2

seconds to remove air from the through holes. The wetted substrate was then soft-etched to remove all foreign material from the copper surfaces, including the activator. Soft-etching was done by immersing the 5 substrate in a solution of 10% H<sub>2</sub>SO<sub>4</sub> and 5% Hydrogen Peroxide at room temperature for 2 minutes, followed by a water rinse.

The substrate was then electroplated as described in the previous examples, producing a strongly bonded, 10 uniform electroplated layer of copper approximately 1 mil thick.

EXAMPLE 6

Direct Pattern Plating Utilizing Cleaner Conditioner and 15 Sodium Carbonate Accelerator but no Permanganate Treatment

An identical substrate was treated as in Example 5 with the only exception being the omission of the initial permanganate step. Following electroplating, the results were as described for Example 4.

20 While it is contemplated as being within the scope of the present invention to form the mildly basic accelerating solutions of a wide variety of alkaline substances, the following examples are listed as being 25 illustrative of the principles of the present invention and are preferred. In order to test the performance of the various alkaline accelerators produced in accordance with the teachings of the present invention two uniform tests were conducted on each. The first test utilized 30 standard FR4-type, copper-clad, double-sided circuit board material approximately 2.5 cm by 5 cm and provided with through holes. Where indicated, the second test utilized unclad ABS plastic panels approximately 1.5 cm by 5 cm which were etched in a solution of chromic/sulfuric acid. 35 Each test was conducted using the following protocol.

First, the substrate was treated with an adhesion promoter through immersion with agitation in a solution of

30 g/l  $\text{KMnO}_4$  and 20 g/l NaOH dissolved in water at room temperature for approximately two minutes, followed by a one minute rinse in water.

Next, the substrate was treated with a 5 cleaner/conditioner through immersion with agitation in a solution of 45 ml/l Shipley brand 1175A Alkaline cleaner conditioner in water at 80°C for 10 minutes, followed by a one minute rinse in water.

Following conditioning, the substrate was exposed to 10 a pre-dip through immersion with agitation in a solution of 280 g/l NaCl, 1 g/l vanillin and 4 ml/l HCl in water at room temperature for 20 seconds. Following the pre-dip the substrate was treated with an exemplary palladium/tin colloidal catalyst in accordance with the teachings of the 15 present invention as discussed above, followed by a one minute rinse in water.

Following activation the catalytically treated substrate was treated with a mildly-basic accelerator through immersion with agitation in a solution of the 20 various combinations of alkaline substances as discussed above at 58°C for 10 minutes, followed by a one minute rinse in water.

Lastly, the accelerated substrate was treated in an acid bath through immersion with agitation in a solution 25 of 10%  $\text{H}_2\text{SO}_4$  at room temperature for three minutes followed by a two minute rinse in water.

Utilizing this exemplary treatment protocol the following tests were conducted to illustrate the effectiveness of the mildly-basic and mildly-basic copper 30 ion containing accelerating solutions of the present invention. It should be noted that the principle evidence of effectiveness of this acceleration treatment is the significantly lowered electrical resistance of the conducting colloidal layer relative to the high resistance 35 of the prior art. Additionally, subsequent plating current densities are significantly lower utilizing the teachings of the present invention and complete direct

electroplating through hole coverage is much quicker, as illustrated in the following non-limiting examples.

EXAMPLE 7

5       Acceleration With Mildly Basic KOH Solution

Five specimens of FR4-type copper-clad, double-sided circuit board material was treated using the above described experimental protocol utilizing an accelerator solution containing 200 g/l of KOH in distilled water. 10 Following this treatment the resistance was measured from side-to-side and averaged 15 ohms.

The catalytically treated and accelerated specimens were subsequently plated as described above utilizing a solution containing 80g copper sulfate, 180g sulfuric acid, and 30 mg chlorine at a temperature of 28° C utilizing current densities ranging from 0.5 A/dm<sup>2</sup> to 1.0 A/dm<sup>2</sup>. It was observed that through hole coverage was completed in approximately 4 minutes at 0.5 amps and in approximately 2 minutes at 1.0 amps.

20

EXAMPLE 8

Acceleration With Mildly Basic KOH Solution Including Copper Ions

As with Example 7, five specimens of FR4-type material were treated using the previously described protocol and an accelerating solution containing 200 g/l of KOH and 2 ml of a solution containing 100g of CuSO<sub>4</sub> in one liter of 10% H<sub>2</sub>SO<sub>4</sub> in distilled water. Following treatment resistance was measured from side-to-side and 30 averaged 10 ohms.

As with the immediately preceding example, the specimens were plated using the same copper plating solution and current densities. Through hole coverage was completed in 3 minutes at 0.5 amps and in 1.5 minutes at 35 1.0 amp.

EXAMPLE 9

Acceleration with Mildly Basic Na<sub>2</sub>CO<sub>3</sub>, Accelerating Solution

An additional five specimens of FR4-type material were treated as discussed above utilizing an accelerating 5 solution containing 300 g/l of Na<sub>2</sub>CO<sub>3</sub> in distilled water. Following treatment resistance was measured from side-to-side and averaged 1.5 ohms.

As with the preceding examples, the specimens were copper plated utilizing the same plating conditions and 10 current densities. Through hole coverage was completed in 15 seconds at 0.5 amps and in 10 seconds at 1.0 amps.

EXAMPLE 10

Acceleration With Mildly Basic Na<sub>2</sub>CO<sub>3</sub>, Solution Including 15 Copper Ions

An identical five specimens of FR4-type material were treated as discussed above utilizing an accelerating solution containing 300 g/l of Na<sub>2</sub>CO<sub>3</sub> and 2 ml of a solution containing 50g of 10% H<sub>2</sub>SO<sub>4</sub> in 1 liter of 20 distilled water. Following treatment resistance was measured from side-to-side and averaged 1 ohm.

The specimens were plated utilizing the same copper plating conditions and current densities. Through hole coverage was completed in 10 seconds at 0.5 amps and in 5 25 seconds at 1.0 amp.

EXAMPLE 11

Acceleration With Mildly Basic K<sub>2</sub>CO<sub>3</sub>, Solution

An additional five specimens of FR4-type material 30 were treated using the above described protocol and accelerating solution containing 390 g/l of K<sub>2</sub>CO<sub>3</sub> in distilled water. Following treatment resistance was measured from side-to-side and averaged 150 ohms.

The treated specimens were plated as discussed above 35 utilizing the same copper plating conditions and current densities. Through hole coverage was completed in 7 minutes at 0.5 amps and in 5 minutes at 1.0 amps.

EXAMPLE 12Acceleration With Mildly Basic K<sub>2</sub>CO<sub>3</sub> Solution Including Copper Ions

Five additional specimens of FR4-type material were  
5 treated as discussed above utilizing an accelerating solution containing 300 g/l of K<sub>2</sub>CO<sub>3</sub> and 2 ml of a solution containing 100g of CuSO<sub>4</sub> in 1 liter of 10% H<sub>2</sub>SO<sub>4</sub> solution. Following treatment resistance was measured from side-to-side and averaged 150 ohms.

10 The specimens were copper plated as discussed above utilizing the same copper plating conditions and current densities. Through hole coverage was completed in 6 minutes at 0.5 amps and in 5 minutes at 1.0 amps.

15

EXAMPLE 13Acceleration With Mildly Basic Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> Solution Including Copper Ions

An additional five specimens of FR4-type material were treated as discussed above utilizing an accelerating solution containing 150 g/l of Na<sub>2</sub>CO<sub>3</sub> and 150 g/l of K<sub>2</sub>CO<sub>3</sub> with 2 ml of a solution containing 100g of CuSO<sub>4</sub> per liter of 10% H<sub>2</sub>O<sub>4</sub> solution. Following treatment resistance was measured from side-to-side and averaged 0.3 ohms.

The specimens were copper plated as discussed above  
25 using the same plating conditions and current densities. Through hole coverage was completed in 5 seconds at 0.5 amps and in 2 seconds at 1.0 amps.

30

EXAMPLE 14Acceleration With Mildly Basic KOH Solution Including Copper Ions

Five specimens of the above described ABS material were treated utilizing the above discussed experimental protocol and an accelerating solution containing 200 g/l of KOH and 2 ml of a solution containing 100g of CuSO<sub>4</sub> in 1 liter of 10% H<sub>2</sub>SO<sub>4</sub> solution. Following treatment

resistance was measured from two points approximately 3 cm apart and averaged 7,000 ohms.

The specimens were copper plated utilizing the previously described copper plating conditions and current densities. Coverage was completed in 8 minutes at 0.5 amps and in 3.5 minutes at 1.0 amps.

EXAMPLE 15

Acceleration With Mildly Basic Na<sub>2</sub>CO<sub>3</sub> Solution Including  
Copper Ions

Five specimens of the above described ABS material were treated using the previously described experimental protocol and an accelerating solution containing 300 g/l of Na<sub>2</sub>CO<sub>3</sub> and 2 ml of a solution containing 50g of CuSO<sub>4</sub> in 1 liter of a 10% sulfuric acid solution. Following treatment resistance was measured at two points approximately 3 cm apart and averaged 1,000 ohms.

The specimens were copper plated utilizing the previously described copper plating conditions and current densities. Coverage was completed in 3 minutes at 0.5 amps and in 1.5 minutes at 1.0 amps.

EXAMPLE 16

Acceleration With Mildly Basic Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> Solution  
Including Copper Ions

An additional five specimens of the previously described ABS material were treated utilizing the above described experimental protocol and an accelerating solution containing 150 g/l of Na<sub>2</sub>CO<sub>3</sub> and 150 g/l of K<sub>2</sub>CO<sub>3</sub> with 2 ml of a solution containing 100g of CuSO<sub>4</sub> in 1 liter of 10% H<sub>2</sub>SO<sub>4</sub> solution. Following treatment resistance was measured at two points approximately 3 cm apart and averaged 500 ohms.

The treated specimens were copper plated utilizing the previously described copper plating conditions and current densities. Coverage was completed in 1.5 minutes at 0.5 amps and in 1 minute at 1.0 amps.

Having thus described the preferred exemplary embodiments of the present invention, it should be noted by those skilled in the art that the disclosures herein are exemplary only and that alternatives, adaptations, and 5 modifications may be made within the scope of the present invention. Thus, by way of example and not of limitation, it is contemplated that different catalyst solution concentrations and alternative noble or precious metals may be utilized to form the uniform, conducting, micro- 10 fine catalytically deposited colloidal layers on the substrates of the present invention. Accordingly, the present invention is not limited to the specific embodiments illustrated herein.

## WHAT IS CLAIMED IS:

1. A mildly basic aqueous accelerating solution for treating the surface of a substrate prior to electroplating.

2. The mildly basic aqueous accelerating solution of claim 1 wherein said solution includes a concentration of copper ions.

10

3. The mildly basic aqueous accelerating solution of claim 2 wherein said concentration of copper ions is dilute.

15

4. A mildly basic accelerating solution for treating the surface of a dielectric substrate prior to electroplating, said accelerating solution comprising:

from approximately 100 grams per liter to 400 grams per liter of at least one alkaline substance selected from 20 the group consisting of NaOH, KOH,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$ ; and water.

25

5. The mildly basic aqueous accelerating solution of claim 4 further comprising a dilute concentration of copper ions.

30

6. The mildly basic aqueous accelerating solution of claim 5 wherein said dilute concentration of copper ions is equivalent to 2 ml of 10%  $\text{H}_2\text{SO}_4$  solution containing from approximately 50 to 100 grams per liter  $\text{CuSO}_4$  per liter of accelerating solution.

35

7. The mildly basic aqueous accelerating solution of claim 4 wherein said alkaline substance is NaOH.

8. The mildly basic aqueous accelerating solution of claim 4 wherein said alkaline substance is KOH.

9. The mildly basic aqueous accelerating solution of claim 4 wherein said alkaline substance is  $\text{Na}_2\text{CO}_3$ .

10. The mildly basic aqueous accelerating solution 5 of claim 4 wherein said alkaline substance is  $\text{K}_2\text{CO}_3$ .

11. The mildly basic aqueous accelerating solution of claim 4 wherein said alkaline substance is  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ .

10 12. A method for accelerating a catalytically treated dielectric substrate prior to electroplating, said method comprising the steps of:

15 forming a mildly basic aqueous accelerating solution comprising from approximately 100 grams per liter to 400 grams per liter of at least one alkaline substance selected from the group consisting  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$ , and a dilute concentration of copper ions; and  
immersing said substrate in said accelerating  
20 solution.

**AMENDED CLAIMS**

[received by the International Bureau on 26 October 1992 (26.10.92);  
original claims 1-11 deleted; new claims 13-32 added;  
claim 12 unchanged (6 pages)]

1. Cancelled
- 5 2. Cancelled
3. Cancelled
- 10 4. Cancelled
5. Cancelled
6. Cancelled
- 15 7. Cancelled
8. Cancelled

9. Cancelled

10. Cancelled

5

11. Cancelled

10 12. A method for accelerating a catalytically treated dielectric substrate prior to electroplating, said method comprising the steps of:

15 forming a mildly basic aqueous accelerating solution comprising from approximately 100 grams per liter to 400 grams per liter of at least one alkaline substance selected from the group consisting NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>, and a dilute concentration of copper ions; and

20 immersing said substrate in said accelerating solution.

25 13. A method for plating a conducting metal onto the surface of a non-conducting substrate, said method comprising the step of:

30 depositing a conducting metal from an electrolyte containing dissolved conducting metal onto a substrate having at least a portion of its surface coated with a substantially uniform conducting layer of colloidal metal which has been treated with a basic accelerating solution incorporating copper ions.

35 14. A method for directly electroplating a metal onto the surface of a non-conducting substrate, said method comprising the step of:

36 passing a current between two electrodes immersed in an electrolyte containing dissolved plating metal, one of said electrodes being said substrate, said substrate having at least a portion of its surface coated with a substantially uniform conducting layer of colloidal metal

which has been treated with a basic accelerating solution incorporating copper ions.

15. The method of claim 14 wherein the treated conducting layer has an electrical resistance of less than 500 ohms.

16. The method of claim 13 further comprising the additional steps of:

10 preparing an aqueous, non-acidic, saturated salt solution;

dissolving approximately 100 g per liter of a noble or precious metal salt in a first portion of said solution;

15 dissolving approximately 500 g per liter of a stannous salt in a second portion of said solution;

combining one part of said first portion with ten parts of said second portion of said solution;

reducing the volume of the combined portions to form a supersaturated concentrated catalyst solution;

20 treating at least a portion of the surface of said substrate with said catalyst solution to deposit a substantially uniform, conducting layer of colloidal metal onto said surface; and

25 treating the deposited conducting layer of colloidal metal with a basic accelerating solution incorporating an alkaline substance and copper ions prior to depositing said conducting metal onto said substrate.

17. The method of claim 16 wherein said noble metal is palladium.

18. The method of claim 16 wherein said alkaline substance is a member selected from the group consisting of NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>.

19. The method of claim 16 wherein said alkaline substance is present in a concentration of approximately 200 grams per liter to 400 grams per liter.

5       20. The method of claim 16 wherein said copper ions are present in a concentration of approximately 75 parts per million.

10      21. The method of claim 16 wherein said copper ions are added to said accelerating solution by adding, per liter of accelerating solution, approximately 2 ml of a solution containing approximately 50 to 100 grams of CuSO<sub>4</sub>.5H<sub>2</sub>O per liter of 10% H<sub>2</sub>SO<sub>4</sub> solution.

15      22. The method of claim 16 wherein said treated conducting layer of colloidal metal has an electrical resistance between approximately 1 ohm and 50 ohms.

20      23. The method of claim 16 wherein said conducting metal is a member selected from the group consisting of copper and nickel.

25      24. The method of claim 14 wherein said current has a density between approximately 0.25 A/dm<sup>2</sup> and 5.0 A/dm<sup>2</sup>.

25      25. A non-conducting substrate having a conducting metal plated surface formed in accordance with the method of claim 13.

30      26. The plated substrate of claim 25 wherein said substrate is a non-clad circuit or a molded circuit.

35      27. A method for forming a substantially uniform, accelerated, conducting layer on at least a portion of the surface of a non-conducting substrate, said method comprising the steps of:

preparing an aqueous, non-acidic, saturated salt solution;

dissolving approximately 100 g per liter of a noble or precious metal salt in a first portion of said solution;

5 dissolving approximately 500 g per liter of a stannous salt in a second portion of said solution;

combining one part of said first portion with ten parts of said second portion of said solution;

reducing the volume of the combined portions to form 10 a supersaturated, concentrated catalyst solution;

treating at least a portion of the surface of said substrate with said catalyst solution to deposit a substantially uniform, conducting layer of colloidal metal onto said surface; and

15 treating the deposited conducting layer of colloidal metal with a basic accelerating solution incorporating an alkaline substance and copper ions.

20 28. The method of claim 27 further comprising the additional step of dissolving approximately 1.5 g per liter of an aromatic aldehyde in said aqueous saturated salt solution prior to dissolving said noble or precious metal salt and said stannous salt in said saturated salt solution.

25 29. A non-conducting substrate having a conducting layer deposited on at least a portion of its surface formed in accordance with the method of claim 27.

30 30. The conducting layer-containing substrate of claim 29 wherein said conducting layer has an electrical resistance between approximately 1 ohm and 500 ohms.

35 31. The conducting layer-containing substrate of claim 29 wherein said substrate is a non-clad or molded circuit.

32. The method of claim 16 further comprising the additional steps of:

applying a photoresist to the accelerating solution-treated layer;

5 imaging said photoresist;

developing the imaged photoresist; and

directly plating a metal onto said surface to provide a pattern plated dielectric substrate printed circuit board.

## STATEMENT UNDER ARTICLE 19

Claims 12 to 32 are present in this application.

Claim 12, which was present in the application as filed, relates to a method for accelerating a catalytically treated dielectric substrate using a mildly basic aqueous accelerating solution containing an alkaline substance and copper ions.

Claims 13 and 16 to 23 relate to a method for plating a conducting metal onto the surface of a non-conducting substrate using the accelerating solution described above with respect to claim 12.

Claims 25 and 26 relate to the plated substrate formed using the method of claim 13. Support for these claims can be found in the specification where at page 1, lines 9 to 12, the invention is described as being directed to both direct electroplating and electroless plating of dielectric base materials. Further description of the method can be found at page 9, lines 1 to 29.

Claims 14, 15 and 24 relate to a method for directly electroplating a metal onto the surface of a non-conducting substrate using the novel accelerating solutions of the present invention. The aspect of direct electroplating is described in detail in the specification, particularly at page 11, lines 6 to 20. Additional support for direct electroplating can be found at page 14, lines 26 to 37, and page 15, lines 1 to 7.

Claims 27 and 28 refer to a method for forming a substantially uniform, accelerated, conducting layer on a non-conducting substrate.

Claims 29 to 31 relate to the substrate with the conducting layer deposited thereon. Support for the formation of a conductive layer can be found in the specification, particularly

at page 15, lines 8 to 30. The overall process is described at page 10, line 27 to line 37, and page 11 lines 1 to 20.

Claim 32 relates to a method for producing a pattern plated dielectric substrate printed circuit board. Direct pattern plating is described in Examples 3, 4, 5 and 6 at pages 25 to 28.

The novel processes and products of the present invention, all of which utilize the basic accelerating solution comprising copper ions, provide heretofore unrealized results in many different respects. Use of the accelerating solution of the present invention enhances the conductivity of the conductive catalyst layer, does not require precise process controls, and can be used in high circuit density applications as well as in molded circuits and multi-layer circuit boards. While applicable to both electrolytic and electroless plating, the present invention produces outstanding results in direct electroplating without conversion treatments, without electroplating solution additives, without requiring high plating current densities or large through-hole diameters and without attacking copper oxide layers. The catalyst layers are more durable than those of the prior art, permitting various processing steps to be performed on the catalyzed substrates, and the resulting metal plating is smooth, uniform and durable.

Applicant requests that the above amendments and Statement Under Article 19(1) be entered into the International Application.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/05084

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C23C 18/18  
US CL : 106/1.18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/1.11; 106/1.23; 106/1.26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
parent: US app. 07/440,661 folc which is US, A, 5,071,517

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
APS, copper sodium hydroxide(p) accelerating K<sub>2</sub>CO<sub>3</sub> or potassium Carbonate or sodium carbonate, copper, and accelerating

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 3,011,920 (C.P. SHIPLEY, JR.) 05 December 1961, See col. 4, line 23, example 7 and col. 6, lines 61-63.	<u>1-4,7</u> 5,6,8-12
X	US, A, 4,311,551 (SYKES) 19 January 1982, See table 1, column 7, lines 36-48, column 8 preparation A, claim 23.	<u>1-7</u> 8-12
X	US, A, 3,340,164 (ZIMMERMAN) 05 September 1967, See column 2.	7
Y	US, A, 3,793,038 (MAGUIRE) 19 February 1974, See entire patent.	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance		
"E" earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"Z"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

27 JULY 1992

Date of mailing of the international search report

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